Colloidal Properties of Iron Oxide in the Removal of Hydrogen Sulphide from Gas

By

FRANK H. DOTTERWEICH

A DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY WITH THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

1937

[Reprinted from the Proceedings of the American Gas Association, Technical Section, October 12, 1938]

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Colloidal Properties of Iron Oxide in the Removal of Hydrogen Sulphide From Gas[1,2]

FRANK H. DOTTERWEICH[3]

An examination of published information on the rating of iron oxide purifying materials for the removal of hydrogen sulphide from gas discloses an unsatisfactory and inconclusive situation. The results obtained by chemical analyses do not form a basis for predicting the efficiency of oxide used and there is no standard test for this which has received universal acceptance. In general, the efficiency is determined by correlating various observations made while fouling the purifying material with hydrogen sulphide. Attempts have been made to govern such tests by scientific considerations, as, for example, in the work by Gordon C. Milbourne(1) with one of the authors of this paper. Various studies have recognized the significance of the capacity and activity of the iron oxide, but a clear cut differentiation of iron oxides based upon these properties has apparently not been attained and the properties are not entirely separable. The work of Milbourne, just cited, emphasized particularly the variable effects which may be produced by humidity. Other factors such as alkalinity and temperature also enter.

In the study to be described, major attention was directed to a correlation of the physical and colloidal properties of the iron oxide with its efficiency in the removal of the hydrogen sulphide. A rapid means for determining the colloidal content of the oxide was first developed. With this available, consideration was then given to the correlation of the observations made by this method with those which involve the interaction of the oxide with hydrogen sulphide in so-called "activity and capacity tests." From the results obtained it is concluded that in order to be satisfactory an iron oxide purifying material must be in the colloidal form.

The study was then extended to an examination of the effect of admixture with other materials. It was noted that in some oxides 11 per cent or more by weight of a suitable aluminum oxide favored higher activity and higher capacity. This information was applied to the beneficiation of a commercial active oxide low in apparent capacity, with the result that the capacity was increased without affecting the apparent activity. The results have been summarized and a chart constructed to permit the prediction of the efficiency of the oxide from a knowledge of its colloid content.

Researches Dealing with the Physical Structure of Iron Oxide

Weyman(2) has shown that ferric hydrates dehydrated at temperatures as high as 650° C. continue to react with dry hydrogen sulphide when cold. From this, he concluded that the chemical activity of the iron oxide is dependent principally on the molecular structure and not on any particular degree of hydration.

Nicolardot's(3) studies indicate that there are at least six modifications of ferric hydrate which exhibit differing solubilities in water and in other physical and chemical properties. Van Beimmelen and Kolb(4) have shown that the water content of iron hydroxide is dependent on (a) the modification which it has suffered on drying, (b) the water vapor content of the atmosphere, and (c) the temperature.

One of the most interesting of these studies, from the standpoint of American gas engineering practice at least, is that of Krause(5) whose work in the peptization of fused ferric oxide may bear some relation to the reactivation of an oxide which has been overheated in a purifier box. Krause has also studied the transformation of the dark reddish brown "ortho-ferric hydrate" to the bright yellow "meta-ferric hydrate."

Weiser(6) in his discussion of the anhydrous and hydrous ferric oxides has made a valuable

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[1] The experimental material presented in this paper forms a portion of the dissertation submitted by Frank H. Dotterweich to the Board of University Studies of the Johns Hopkins University in partial fulfilment for the degree of Doctor of Philosophy.

[2] In accordance with commercial practice the ferric compound or compounds generally used for the removal of hydrogen sulphide from gas will be denominated "iron oxide" in this paper.

The term "aluminum oxide" is used in a sense analogous to that connoted by the term "iron oxide."

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contribution by correlating their color with the particle size. He reports that the hydrous oxide can be prepared in a variety of colors similar to those of the anhydrous oxide and that it seems that the difference in color is due to a difference in the size of the particles.

Mott(7), Anderson(8) and Wohler and Andrea(9) agree that in the anhydrous oxide the color varies with increasing particle size from yellow to red, the red being the largest.

Keane(10) has noted that finely divided ferric oxide tends to agglomerate and this is overcome in the so-called Mars Pigments by the presence of aluminum oxide.

If the activity of a purification material may be correlated to the particle size by observing the color of the material, it is possible that its activity may be predicted from color considerations. However, this is impossible because of the varying quantities and types of inert materials such as impurities and salts which are normally present in purifying material and may alter the color.

The Effect of Temperature on the Physical Structure of Iron Oxide

In a consideration of the physical structure of iron oxide the effect of temperature should be included because this oxide may lose its colloidal properties on heating.

Steinkopff(11) has stated that on heating amorphous particles of ferric oxide they became crystalline. He does not include aluminum oxide in the group of oxides that exhibit this phenomenon.

Bunte(12) and others have shown that the rates of reaction of iron oxide with hydrogen sulphide and with oxygen (during revivification) are increased as the temperature rises to a maximum and that the rates then decrease.

Murphy(13) has prepared a gas purifying material which he calls "superactive." He passed the material through a 200-mesh screen and then heated it to a temperature of 200° C. or 300° C. or 500° C., then allowed the material to cool, and stored it for use.

Gedel(14) has shown that the moisture content of freshly precipitated ferric hydroxide varied with the temperature and the humidity of the atmosphere so that he never obtained a completely similar product twice.

Researches on the Effect of Water in Iron Oxide

It is probable that the activity of the interaction between iron oxide and hydrogen sulphide is closely related to physical structure of the iron oxide-water system. Other factors probably enter and all may be affected by temperature conditions.

That the presence of water is an important condition for the reaction between hydrogen sulphide and iron oxide has long been understood, and the addition of water and steam to iron oxide boxes used commercially for the removal of hydrogen sulphide has been practiced for many years.

Brescius(15) in 1869 published researches to show that dry hydrogen sulphide exerts no action on dry ferric oxide and that moist hydrogen sulphide acts on dry ferric oxide only slowly, and with small heat generation.

Dunkley and Leitch(16) found that the activity of iron oxides was affected by the water content, and that each oxide has a best range of water content, any increase or decrease beyond this range decreasing the activity. The optimum content and range depended upon the particular oxide, thus, a dark red or black oxide was found to be more sensitive to changes in water content than the yellow or the yellowish brown oxides. They noted that an oxide which had been dried and then remoistened regained the activity corresponding to its water content only very slowly.

Bunte(12) and others stated that in general an increase in moisture content increases the rate of hydrogen sulphide absorption while the revivification process is only slightly or adversely affected.

Huff and Milbourne(1) have conducted an extensive study of the effect of humidity conditions in the dry iron oxide box purification of gas. Research shows that the humidity of the gas during the fouling and revivification has an important influence on the results obtained.

The Effect of Alkalinity

Ferric oxide when in the colloidal state is known to carry strong positive electrical charges scattered over its extensive surface. An increase in this charge should cause the particles to repel each other with greater force while a neutralization of this charge by negatively charged particles may cause this repulsion to be reduced. Certain colloids carrying these electrical charges may be treated with chemicals which yield certain favored positive or negatively charged ions to increase or decrease this repulsion with an accompanying increase or decrease in surface content.

Louis Gedel(14) has made a very valuable study of the great difference in the action of purifying oxide between slightly alkaline and slightly acid conditions.

Stone(17) stated in his report that alkalinity increased the efficiency of many oxides, and concluded that an alkalinity of about 2 per cent (figured as $CaCO_3$) gave the best results. Dunkley and Leitch(16) reported that the addition of soda to a natural oxide greatly increased its ability to remove the last traces of hydrogen sulphide.

Bunte(12) and others working with bog ores from Holland and Germany have reported that alkaline additions had no appreciable effect on the activity. Their experiments indicated that alkalinity made little change in the activity of a highly active synthetic oxide containing appreciable amounts of aluminum oxide.

It is beyond the scope of this presentation to enter into a discussion of many other interesting and important researches upon iron oxide and the various factors governing its ability to remove hydrogen sulphide from gas. Further information with citations to a number of these will be found in another treatise by one of the writers(18).

Proposed Testing Methods

Malachite green has been used in the determination of the colloidal properties of clay, and this use suggested that it might be employed to develop a practical and rapid means for the determination of colloidal properties of iron oxide. It was soon found necessary to modify this test to overcome or at least minimize the disadvantages or possible errors inherent in such a method with respect to (a) calcium ion effect upon the dye and (b) the non-uniform adsorption due to varying pH of the solution.

Ashley's(19) work on the colloidal properties of clay has shown that calcium and alkaline salts affect the adsorption of malachite green. He therefore limited the use of this test to high grades of clay which were not contaminated by lime or alkaline ingredients.

Moore and others(20) in their work on the determination of the colloidal content of clay with malachite green appear to have overcome the effect of calcium by precipitating this in the form of the insoluble calcium oxalate by the addition of sodium oxalate. They have also shown that an excess of sodium oxalate did not affect the malachite green. The present study gave results in agreement with the statement that sodium oxalate does not affect the dye, but experiments have shown that the shift of the hydrogen ion concentration of the solution, which may be brought about by the addition of alkaline salts, will cause a given amount of colloid to adsorb a greater quantity of dye at a lower hydrogen ion concentration of the solution.

Researches by Weiser(21) and Gordon(22) have also indicated that the adsorption of a dye by a hydrous oxide is dependent upon the pH of the solution. Weiser(23) has shown in his work with alizarin dyes that the hydrous oxides adsorb the sulfate and the oxalate radical, but that the dye is adsorbed in preference to the sulphate or oxalate when both are in the bath, except in very acidic baths in which the sulphate and oxalate replace the dye.

The disadvantages of the foregoing tests when applied to the study here presented appear to lie in difficulties resulting from varying calcium ion effects in the solutions of varying hydrogen ion concentrations in contact with various purifying masses containing soluble calcium and alkaline salts.

In the tests of previous workers no provision appears to have been made to secure constant hydrogen ion concentration in the test solutions.

Dye Adsorption Test Adopted

A buffer solution containing so much acid that the addition of the basic dye gave a solution which was still acidic was chosen. This solution contained 4 parts of 1 N. potassium oxalate and 1 part of 1 N. oxalic acid, giving a solution whose pH was approximately 5.5. This buffer was chosen for the following reasons:

1. The oxalate radical should precipitate the calcium present in the form of the insoluble calcium oxalate, thereby eliminating the calcium effect upon the dye.

2. The capacity of the buffer should tend to hold the hydrogen ion concentration of the solutions approximately constant, eliminating the possibility of non-indicative dye adsorption due to varying hydrogen ion concentration of the solution.

In order to investigate the adsorption of malachite green in baths containing various hydrogen ion concentrations, an iron oxide high in colloid content was treated as follows:

The adsorptions of malachite green by one-gram samples of the oxide were measured, using 50 c.c. of buffer solution and various portions of 1 N. oxalic acid and 50 c.c. of standard dye solution (containing 300 mg. of malachite green). It was found that the adsorption decreased with increasing acidity until a minimum adsorption of 117 milligrams of dye per gram of oxide is reached with the addition of 30 c.c. of 1 N. oxalic acid. Further addition of acid gave a decrease in color until the dye was apparently destroyed with the addition of 60 c.c. of 1 N. oxalic acid.

Moore and others(20) observed that variations in the size of the samples used with a constant initial amount of dye showed that distribution between the colloidal surface and the solution was playing a part in determining the amount of dye adsorbed. They overcame this difficulty by keeping a constant amount of dye in solution after adsorption.

In the present study it was observed that practically all the purifying materials generally accepted as good adsorbed from 300 mg. to 600 mg. of dye per gram of oxide. By keeping a minimum of 150 mg. of dye in solution after adsorption there appeared to be no error due to distribution effects.

The following standard procedure was adopted:

Into a 200 c.c. wide mouth bottle provided with a rubber stopper 50 c.c. of buffer[4] solution were placed; then 1 gram of the sample was added. The solution was shaken at once by hand to prevent coagulation and then placed in a mechanical shaker for 1 hour to precipitate any calcium present. 125 c.c. of standard dye solution[5] were then added and the whole was again shaken for 1 hour. The sample was allowed to settle over night. On the following day a convenient amount of the supernatant liquid was taken out by a 10 c.c. pipette, the end of which was inserted to approximately one-fourth the depth of the liquid; this portion of the solution was placed in a test tube and corked until the adsorption was determined by color comparison.

For color comparison, it was found that 1 c.c. of the standard solution diluted to 200 c.c. gave the most satisfactory results when a beam of white light was passed up through exactly 10 c.c. of this solution in one of a pair of matched Nessler tubes. Exactly 1 c.c. of the sample removed from the test bottle was transferred to a 100 c.c. graduate and diluted until a perfect match was obtained with the color obtained by diluting the standard solution.

The dilution factor was first determined approximately, then the determination was repeated by approaching this approximation by the addition of 1 c.c. of water at a time. The dilution at which a further addition of water gave an indication of a lighter color than the standard was chosen as the final reading.

The following will illustrate the data and the calculations:

Sample No. 23 Date, December 10, 1936.
c.c. of Standard Solution taken: 125
Concentration of Standard Solution: .006 grams malachite green per c.c.
Total Volume of Liquor at the end of the Adsorption: 175 c.c.
Dilution of Standard: 200 times
Dilution of Liquor to match: 32 times
Total Dye Taken: $125 \times .006 = .750$ grams
Total Dye Remaining: $175 \times \frac{32}{200} \times .006 = .168$ grams
Dye Adsorbed: $.750 - .168 = .582$ grams

Preparation of Samples

A substantially complete representation of the materials used in present-day dry box purification was sought by solicitation from consumers and is believed to have been obtained.

The samples selected for this study, twenty-five in number, are indicated on Table 1. They represent five different manufacturers' products and others whose origins were not stated. The color, form in which received, and consumer's rating are also given in the table.

All samples not received in the fluffed form (i.e., not dispersed over a carrier) were ground in a mortar and pestle to pass a 60-mesh sieve and were then heated at 110° C. for two hours. Ample free surface was provided to insure complete drying at this temperature. The oxide samples were then placed in tightly corked bottles and kept there until required.

The fluffed samples were screened to remove the shavings used as carriers and then treated in a manner similar to the unfluffed samples. Oxides of manufacturer "C," No. 8 and No. 9 with "activitated" and "ordinary" ratings, respectively, after separation from the shavings appeared to be the same oxide, but No. 8 contained larger amounts of lime than No. 9. The lime content of No. 8 was so high that it was necessary to wash it in order to secure a fair sample of the oxide.

Determination of Alkalinity of Ferric Oxide Purifying Material

That the alkalinity of an oxide affected its ability to remove hydrogen sulphide from gas has been recognized for a long time. It was therefore necessary to determine the alkalinity of the samples so that this might be correlated with the dye adsorption, activity and capacity of the purifying material.

The alkalinity was determined as follows: A 1 gram sample of the oxide was placed in a 200 c.c. bottle containing 50 c.c. of distilled water and shaken for one hour. This was allowed to stand until a clear solution resulted; then a 10 c.c. portion of the clear liquid was withdrawn and titrated with dilute hydrochloric acid, using methyl orange as an indicator. From this titration the alkalinity was calculated as per cent by weight of sodium carbonate.

Leaching of Ferric Oxide Purifying Material

To study the effect of leaching on ferric oxide purifying material, the samples to be leached were treated as follows:

About 30 grams of the purifying material were placed in a large beaker, distilled water was added, and the whole was stirred vigorously. The

[4] Buffer solution: 1 part of 1 N. oxalic acid to 4 parts of 1 N. patassium oxalate.
[5] Standard Dye Solution: 6 grams of malachite green oxalate in 1000 c.c. of distilled water.

TABLE I

Oxide Number	*Manufacturer*	*Color*	*Form Received*	*Consumer's Rating*	*Apparent Manufacturer*
1	A	Light brown	Unfluffed	Good	
2	B	Dark brown	"	"	
3	A	Light brown	"	"	
4	D	Brown	Fluffed	———	
5	C	"	"	———	
6	A	Light brown	Unfluffed	Good	
7	B	Dark brown	"	"	
8	C	Brown	Fluffed	"	
9	C	"	"	"	
10	—	Dark brown	Unfluffed	Fair	B
11	—	Yellow	"	"	A
12	—	Dark brown	"	"	B
13	—	Light brown	"	Good	A
14	—	Dark brown	"	"	B
15	*	Yellow	"	Indifferent	
16	B	Dark brown	"	Good	
17	A	Light brown	"	"	
18	*	Yellow	"	Indifferent	
19	*	"	"	"	
20	—	Dark brown	"	———	B
21	*	Yellow	"	Indifferent	
22	Baker's	Red	"	———	
23	A	Light brown	"	Good	
24	E	"	"	"	
25	D	"	"	"	

*Apparently natural oxides.

mixture was allowed to settle and the clear solution siphoned off. This procedure was repeated three times. The washed oxide was placed in a drying oven and dried at 110° C. for a period of two hours, then passed through a 60-mesh sieve.

Hydrogen Sulfide Test Adopted

As one objective was the correlation of the reactivity of iron oxide in removing the hydrogen sulfide from gas with the colloid content of the oxide, it was necessary to adopt a test for the determination of this activity.

An endeavor to determine the reactivity by the Dunkley and Leitch method(16) met with difficulty in that the results obtained were not consistent. This method was then modified, by maintaining the flow of foul gas constant through the sample and noting the time elapsing before hydrogen sulphide appeared at the outlet.

The samples of oxide and sawdust[6] were brought approximately to the equilibrium moisture content by placing them for two weeks in desiccators containing distilled water. The samples were fouled by gas, at the rate of 3.6 cubic feet per hour, containing 100 grains of hydrogen sulphide per 100 cubic feet of city gas. The samples after fouling were returned to the desiccators and allowed to revivify over night.

The next day the test was repeated until six consecutive daily tests were obtained with this flow. The rate of flow was then increased to 7.2 cubic feet of gas per hour and three daily consecutive tests were conducted. Finally, the rate was increased to 10.8 cubic feet per hour and three daily consecutive tests obtained. From these data the average grains of hydrogen sulfide taken up per gram of oxide was calculated. This figure was used to represent the reactivity of the oxide.

It should be noted that this test involved certain capacity considerations not found in the original Dunkley and Leitch test. The amount of hydrogen sulfide actually decomposed is, however, so small that very little heat was evolved and much of this was carried away at once by the gas current. By returning the samples to the desiccators for revivification and daily fouling, the ability of an oxide to regain its moisture content was involved. Should this ability to adsorb water be a criterion of the colloid content, some correlation of these factors may explain this phenomenon.

A general description of the apparatus and a detailed account of certain parts are given on following page.

General Description of Apparatus (Figure 1)

The gas from the city supply was forced through the apparatus by the pump (b). The pump was connected by a bypass in which was a needle valve (c) by which the rate of flow was

[6] Screened through a 20 mesh sieve.

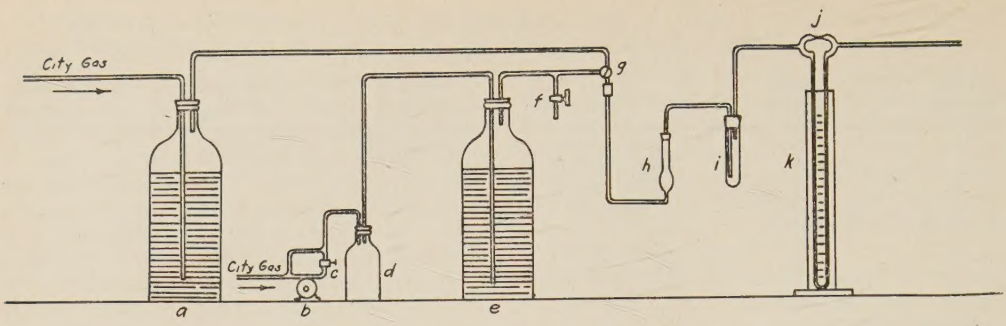

Figure 1. Diagrammatic sketch of apparatus

governed. A bottle (d) served as a trap between the pump and the sulfiding bottle (e). This one-gallon bottle was three-fourths filled with a solution of sodium sulfide and sodium bicarbonate as suggested by Jacobson (24). The desired concentration of hydrogen sulfide in the gas stream was obtained by varying the proportions and concentrations of the sodium salts until exactly 100 grains of hydrogen sulfide per 100 cubic feet of city gas was obtained.

The gas containing hydrogen sulfide then was passed to the oxide testing tube (h) described later (see Figure 2), then to the indicator tube (i), a test tube five-eighths of an inch in diameter containing 10 c.c. of a very dilute solution of potassium permanganate.[7] The inlet of this tube dipped into the solution about one-half inch. From the indicator tube the gas passed through the calibrated flow meter (k), consisting of a short piece of capillary tubing (j) with its ends connected to a water manometer tube with a range of about 20 inches of water pressure. For purging the apparatus, city gas was passed through a one-gallon bottle three-fourths filled with water to saturate the gas at room temperature with water vapor. The purging apparatus was connected to the train by the three-way stopcock (g). A gas sampling connection was inserted at (f) for hydrogen sulfide tests.

The hydrogen sulfide concentration was checked daily with the Tutwiler apparatus. The time of contact was ascertained with the aid of a stopwatch.

Detailed Description of Oxide Testing Tube
(Figure 2)

The oxide testing tube, the straight portion of which was five-eighths of an inch in diameter and approximately four inches long, was filled with glass wool at (j) on which was poured a one-half inch layer of cracked glass (i). This cracked glass had been passed through a 20-mesh sieve but was retained on a 40-mesh sieve. Above the glass was a porcelain filter plate (h), the

[7] Six drops of normal potassium permanganate to 360 c.c. of distilled water.

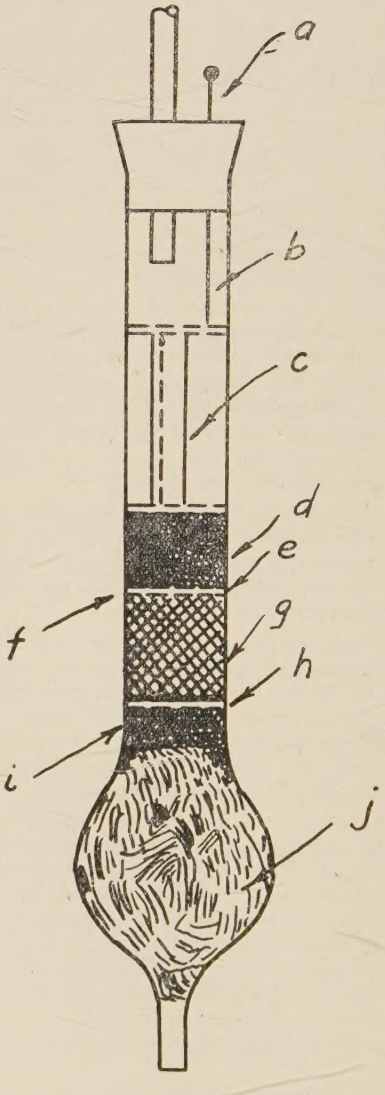

Figure 2. Oxide testing tube

edge of which was ground on an emery wheel until the plate fitted snugly into the tube. Upon the filter plate was placed a mixture (g) of 1 gram of the oxide with ½ gram of sawdust that had been screened through a 20-mesh and over a 40-mesh sieve.

After two weeks in the desiccator the oxide and sawdust were mixed with a spatula and poured into the tube. The tube was held in a vertical position while being filled and rotated slowly around its vertical axis and tapped. After the oxide had been placed in the tube, there was added a thin layer of sawdust (f) whose thickness was varied slightly from time to time to make up the difference in volume between dense and light oxide and so bring the surface always to a fixed level in the tube. Upon the sawdust was placed a porcelain filter plate (e) ground to fit snugly. Upon this plate was placed six grams of ground glass (d).

A spacer (c) was placed above the ground glass. This spacer was made from two porcelain filter plates, ground circumferentially to fit loosely in the tube, separated by a piece of glass tubing about 1½ inches long, the whole being held together with a piece of fine copper wire. This spacer prevented the ground glass from being carried over into the indicator tube by high rates of flow. A free space (b) about ½ inch along the axis of the tube was allowed to intervene between the stopper and the top of the spacer. A small hat pin (a) projecting through the rubber stopper was adjusted to maintain this interval.

These conditions were followed closely from experiment to experiment to insure uniform packing conditions.

Complete details of the testing procedure will be found in another treatise by one of the writers (18).

The Capacity of Iron Oxide Purifying Material

To determine the capacity of an iron oxide for the removal of hydrogen sulphide from gas, the original Kunberger test (25) was used.

This was selected because it is a capacity test and should show the undesirable property of extremely active oxides in over-heating unless treated with satisfactory amounts and types of inerts.

The capacities reported were the sum of four consecutive daily foulings. A general description of the apparatus and procedure may be found in the Gas Chemists' Handbook (26).

Determination of the Per Cent of Ferric Oxide in Purifying Material

To correlate the colloid content, activity, and capacity on a 100 per cent ferric oxide basis, the per cent of ferric oxide in the purifying mass was determined as described below. This permits the determination of aluminum oxide also.

To a platinum crucible half filled with sodium carbonate, approximately one quarter of a gram of the oxide was added. The crucible containing the sodium carbonate was weighed accurately before and after the addition of the sample. The crucible was then three-fourths filled with sodium carbonate and the mass fused in an electric furnace.

The fused sample was then placed in a beaker and dissolved in about 100 c.c. of distilled water to which about 20 c.c. of concentrated hydrochloric acid was slowly added. The solution was filtered and then made up to 300 c.c. This was divided into 200 c.c. and 100 c.c. portions. The 200 c.c. was heated to boiling and made alkaline with hot potassium hydroxide; the precipitated ferric hydroxide was washed with hot water and the filtrate and washings saved. This precipitate was dissolved in hydrochloric acid and the iron then precipitated with ammonium hydroxide. This was boiled, filtered, washed free of chlorides, ignited and weighed as ferric oxide.

The filtrate from the iron precipitate was made acid with nitric acid and the aluminum precipitated with ammonium hydroxide. This was filtered, washed free of chlorides, ignited, and weighed as aluminum oxide.

A knowledge of the content of aluminum oxide and ferric oxide contents permitted the oxides to be divided into two groups, one containing more than 11 per cent aluminum oxide and one containing less than 11 per cent aluminum oxide. The two groups gave different properties with respect to activity and capacity with hydrogen sulphide.

Correlation of Colloid Content, Activity, and Capacity on a 100 Per Cent Ferric Oxide Basis

The experimental work has been condensed and is reported in Table II. Group 1, consisting of oxides containing more than 11 per cent by weight of aluminum oxide on an iron oxide-aluminum oxide basis, showed variations in dye adsorption from 105 mg. to 1,570 mg. per gram of oxide with corresponding activity of nil and 21 for oxides No. 21 and No. 11, respectively. The capacities of these oxides were also the maximum and minimum of this group, being 140 for oxide No. 21 and 285 for oxide No. 11.

In group 2, oxides containing less than 11 per cent by weight of aluminum oxide on an iron oxide-aluminum oxide basis, there is a favorable relation between dye adsorption varying from 743 mg. to 25 mg. The activity varies from 12 to nil.

These data are shown in Figure 3. When reduced to a 100 per cent ferric oxide basis, each group gives a distinctive curve. Both curves, however, show increasing activity with decreas-

TABLE II

Sample Number	*Capacity/g. Oxide, % H_2S Removed*	*Activity/g. Oxide, Milligrains H_2S*	*Dye Adsorbed /g. Oxide, mg.*	*% Fe_2O_3/ g. Oxide*	*Capacity/g. Fe_2O_3, % H_2S Removed*	*Activity/g. Fe_2O_3, Milligrains H_2S*	*Dye Adsorbed /g. Fe_2O_3, mg.*
				Group 1			
11	95.9	7.1	530	33.7	285.0	21.0	1,570
1	122.3	10.2	571	54.0	227.0	18.9	1,056
3	118.1	10.1	550	57.5	208.0	17.5	956
13	108.9	9.1	566	55.1	197.4	16.9	1,030
6	105.0	7.9	556	58.3	180.0	13.6	955
23	109.9	6.9	550	60.3	182.0	11.4	912
17	104.0	6.8	524	59.8	173.5	11.4	876
25	84.4	4.3	435	44.7	188.4	9.6	973
24	136.1	6.4	556	72.8	187.1	8.8	765
18	132.5	4.4	251	81.6	162.1	5.4	307
15	132.2	3.4	120	76.0	174.0	4.5	158
19	156.4	3.0	225	82.3	190.0	3.6	274
21	73.2	—	52	49.3	140.7	—	105
				Group 2			
2	74.0	9.2	571	77.0	96.3	12.0	743
7	73.5	8.8	550	81.8	90.0	10.8	673
14	90.4	6.2	503	77.8	116.0	8.00	646
20	92.9	6.4	512	81.3	114.2	7.9	629
16	92.3	6.3	477	82.4	112.0	7.7	580
10	88.9	6.2	498	87.5	102.2	7.1	570
12	84.7	5.8	488	86.3	98.3	6.7	566
5	102.2	2.3	293	61.8	165.5	3.7	475
4	91.0	2.1	250	59.3	153.6	3.5	421
8	85.0	2.5	409	78.6	108.0	3.2	520
9	96.5	2.7	382	86.8	111.0	3.1	440
22	118.4	—	25	100.0	118.4	—	25

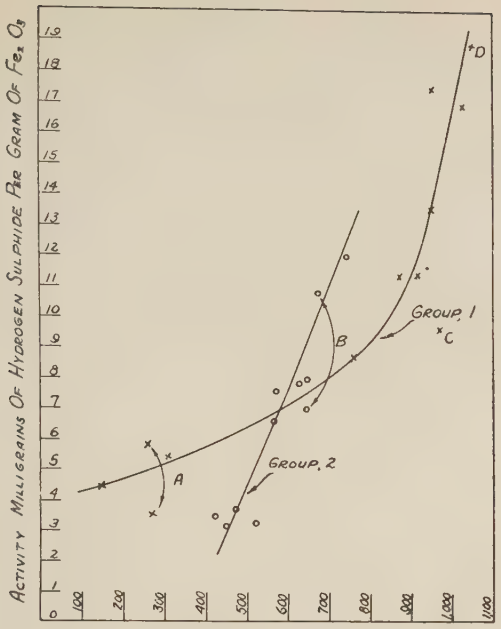

Figure 3. Milligrams of malachite green adsorbed per gram of Fe_2O_3

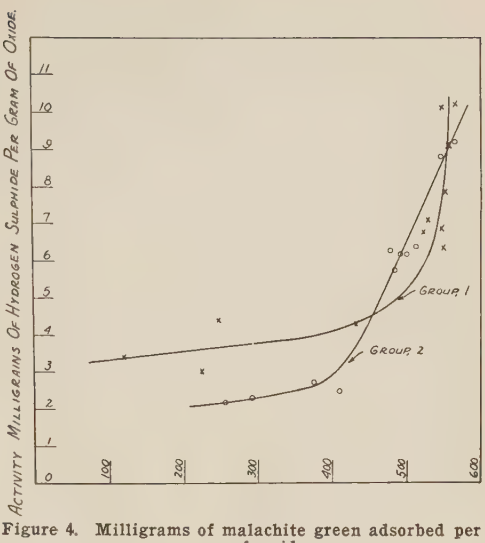

Figure 4. Milligrams of malachite green adsorbed per gram of oxide

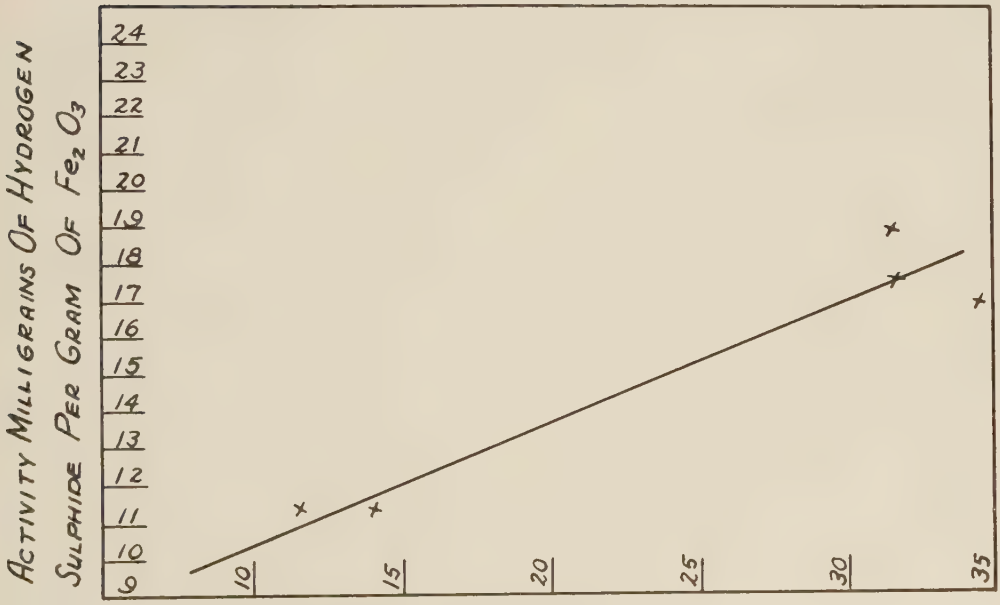

Figure 5. Per cent by weight of Al_2O_3

ing particle size. There is not so pronounced a change in the slopes of the curves as is noted with the curves resulting from activity and dye adsorption of the oxides as received, Figure 4.

Although the points as plotted (Figure 3) do not fall directly on the curve in group 2 by varying the alkalinity, they apparently may be made to do so. This is illustrated by the positions at "B" which an oxide may take when the alkalinity is varied by washing. Oxide No. 7, as shown, with an alkalinity of 7.05, gave an activity of 10.8 and a dye adsorption of 673 mg. On washing, the alkalinity was reduced to 3.08, the activity to 7.0, and the dye adsorption to 640 mg. It appears, therefore, by a small reduction in alkalinity of the original sample this could be made to fall upon the curve.

For group 1, several points do not fall upon the curve shown in Figure 3. This group contained samples having more than 11 per cent by weight of aluminum oxide on the basis previously explained. An examination of the data suggests that as the percentage of aluminum oxide is increased the effect of alkalinity on activity is decreased until a percentage is reached where further reduction in alkalinity may not affect the activity.

As an example, oxide No. 19 had a percentage of aluminum oxide of 18. With an alkalinity of .87 the activity was 3.6 and the dye adsorption 261 mg.; an increase in alkalinity to 5.28 gave a dye adsorption of 273 mg. and an activity of 5.8. These variations in activity are shown at "A" in Figure 3. Apparently a variation in alkalinity of this sample would place it on the curve. However, oxides No. 25 and No. 1 ("C" and "D," Figure 3) with aluminum oxide percentages of 23.5 and 35.3 over the ranges tested, gave constant activity with variations in alkalinity.

Table III shows oxides with somewhat constant particle size, but with various activities and percentages of aluminum oxide. These results are plotted in Figure 5. It will be noted that an increase in the percentage of colloidal aluminum oxide mixed with the colloidal ferric oxide causes an increase in the activity. It follows that the points plotted in group 11, Figure 3, may be made to fall on the curve by varying the percentage of aluminum oxide in the sample.

Figure 6 shows the effect of decreasing particle size on the capacity when these factors are reduced to a 100 per cent ferric oxide basis. Figure 7 gives curves resulting from plotting the capacities of the oxides as received.

Group 2, containing oxides with less than 11 per cent by weight of aluminum oxide gave decreasing capacity with decreasing particle size. Oxide No. 7, a member of this group, on washing, decreased in alkalinity from 7.05 to 3.08 with an increase in capacity from 90 to 117 as indicated at "B" on Figure 6. This is not in accord with the theory that increased alkalinity increases the capacity.

Group 1, containing oxides with more than 11 per cent aluminum oxide gave increasing capacity with decreasing particle size. Oxide No. 19 of this group, reported as indifferent in industry, when treated with 5 per cent by weight of sodium carbonate had an increase in capacity from 190 to 201 ("A" Figure 6).

Table III gives five oxides with approximately constant particle size, but with various percentages of aluminum oxide and ferric oxide and with various capacities. These data are shown in Figure 8. Increases in the percentage of aluminum oxide increase the capacity.

TABLE III

Sample Number	*% Al_2O_3*	*% Fe_2O_3*	*Capacity/g. Fe_2O_3, % H_2S Removed*	*Activity/g. Fe_2O_3, Milligrains H_2S*	*Dye Adsorbed /g. Fe_2O_3, mg.*
13	34.5	65.5	197.4	16.9	1,030
3	33.4	66.6	208.0	17.5	956
1	33.2	66.8	227.0	18.9	1,056
17	18.7	81.3	173.5	11.4	876
23	13.2	86.8	182.0	11.4	912

Oxide No. 11 was not plotted on the curve mentioned. This oxide as received contained 33 per cent by weight of ferric oxide; when calculated to a ferric oxide-aluminum oxide basis the composition was 38 per cent aluminum oxide and 62 per cent ferric oxide. When the activity and capacity were compared on a 100 per cent ferric oxide basis these were found to be 21 and 285 respectively, the maximum results obtained. This suggests that aluminum oxide and ferric oxide in proportion by weight of one to two may be desirable.

The dye adsorption of this sample was 1,570 mg. on a 100 per cent ferric oxide basis. This is high and may be explained by assuming that the aluminum oxide also adsorbs the dye. (Aluminum oxide is also charged positively.) No deduction was made for the amount of dye pre-

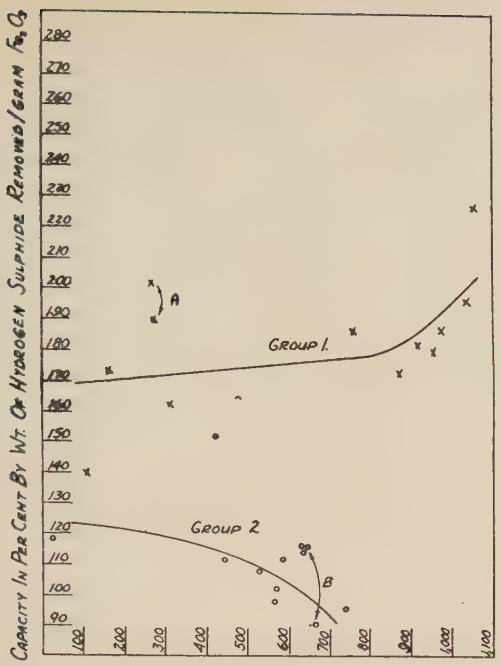

Figure 6. Milligrams of malachite green adsorbed per gram of Fe_2O_3

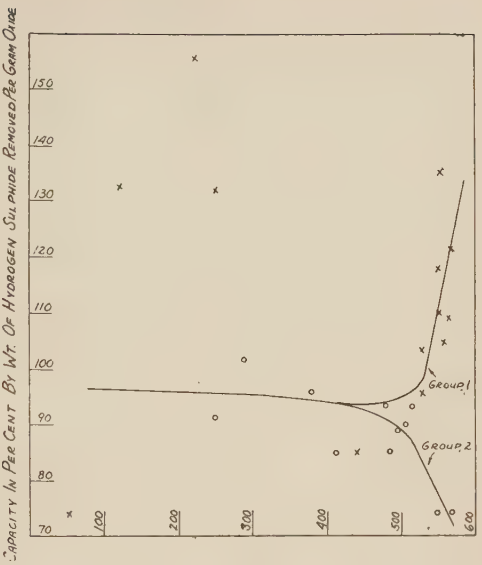

Figure 7. Milligrams of malachite green adsorbed per gram of oxide

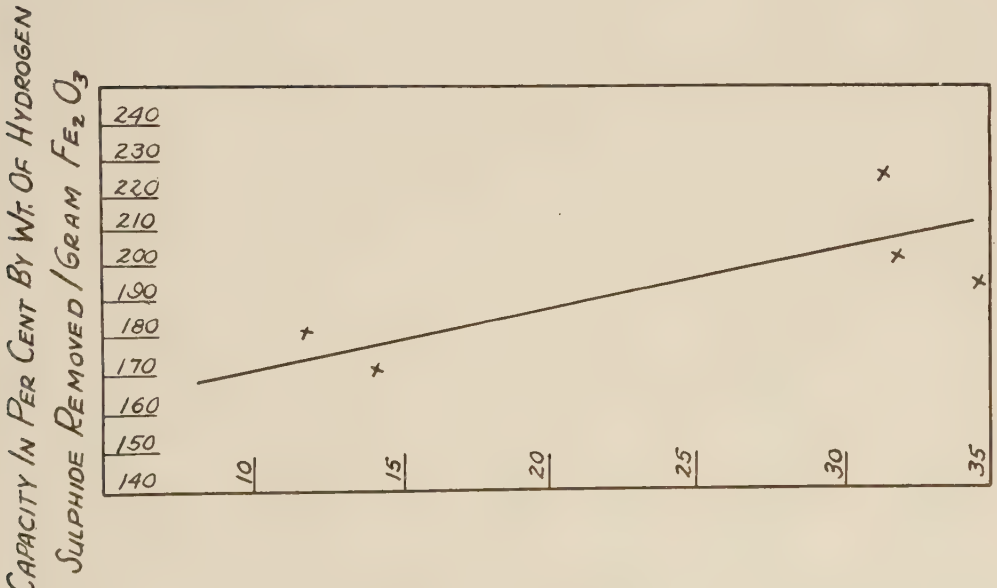

Figure 8. Per cent by weight of Al_2O_3

sumably adsorbed by the aluminum oxide. It appears evident that the presence of this oxide increases activity and capacity and therefore a measurement of the total adsorption is desirable for rating an oxide even though the aluminum may not react chemically with hydrogen sulphide.

The Effect of Heat on Ferric Oxide

In the hope of explaining some of the phenomena of over-heating of an oxide in a purifying box, and to examine the destructive action of heat upon the colloidal properties of the iron oxide, samples were heated in an electric furnace at 550° C. for a period of one hour, allowed to cool, and then passed through a 60-mesh sieve.

The result of this treatment on sample of No. 3, No. 2 and No. 19 is shown in Table IV. In all cases the heating to 550° C. caused a marked reduction in activity and colloid content. Sample No. 2 was affected the most, its activity being reduced to approximately 27 per cent of its original value. Oxides No. 3 and No. 13 were reduced to 34 per cent and 30 per cent, respectively, of the original activity.

Accompanying this decrease in activity and colloid content was a marked change in the color of the oxide. Sample No. 3 turned from a light brown to a dark brown, oxide No. 2 from a dark brown to a very dark reddish brown, while oxide No. 19 changed from yellow to a bright red.

Table V shows the effect of heating on capacity.

The oxides No. 2 and No. 3, very active oxides with high colloid content, had their capacity reduced greatly by heating. It will, however, be noted that the capacity increased as the sample was fouled from day to day. This suggests that the water content of highly colloidal oxides is seriously affected by heating. The reduction in capacity cannot be accounted for by increased particle size alone because oxides with low colloid content still gave high absorptions. Thus oxide No. 19, as shown in Table V, lost little of its capacity for hydrogen sulfide on heating, although its colloid content was reduced.

THE APPLICATION OF PARTICLE SIZE TO THE PURIFICATION OF GAS AND TO THE RATING OF IRON OXIDE PURIFYING MATERIALS

It may be recalled that oxide No. 2 of Group 2 was high in colloidal ferric oxide and low in content of inert material. When this oxide was fouled under the test conditions described in this presentation, the particles apparently agglomerated and the capacity was low. To show the effect of the addition of various types of inerts to this oxide the following tests were conducted.

The oxide was mixed with equal quantities of powdered Albany clay high in aluminum oxide. Daily fouling tests were conducted with this oxide and also with this oxide mixed in a proportion of 3 grams of oxide to 5 grams of sawdust as suggested by Seil(27) in his modified Kunberger test.

TABLE IV

Sample Number	*Alkalinity, % by Wt. Na_2CO_3*	*Activity—Milligrains*		*H_2S/g. Oxide*		*Dye Adsorbed/ g. Oxide, mg.*
		3.6 Cu.Ft./Hr.	*7.2 Cu.Ft./Hr.*	*10.8 Cu.Ft./Hr.*	*Mean*	
3	5.06	9.4	11.2	10.5	10.1	550
3 @ 550*	4.63	3.4	3.6	3.3	3.4	300
2	5.84	8.1	12.2	8.4	9.2	571
2 @ 550*	2.10	3.1	2.4	1.5	2.5	277
19	.87	3.4	2.4	2.7	3.0	225
19 @ 550*	.44	.9	1.0	.6	.9	52

*Sample previously heated to 550° C. for one hour.

TABLE V

Sample Number	*Alkalinity, % by Wt. Na_2CO_3*	*Capacity/g. Oxide—% by Wt. H_2S Removed*					*Dye Adsorbed/ g. Oxide, mg.*
		Daily Fouling, No.					
		1	*2*	*3*	*4*	*Total*	
3	5.06	32.70	28.90	28.21	28.30	118.11	550
3 @ 550*	4.63	5.42	6.02	6.80	8.00	26.24	300
2	5.84	18.26	18.60	17.16	20.00	74.02	571
2 @ 550*	2.10	3.50	7.00	4.20	15.80	30.50	277
19	.87	53.02	41.98	32.35	29.34	156.69	225
19 @ 550*	.44	51.40	48.80	34.66	19.10	153.96	52

*Sample previously heated to 550° C. for one hour.

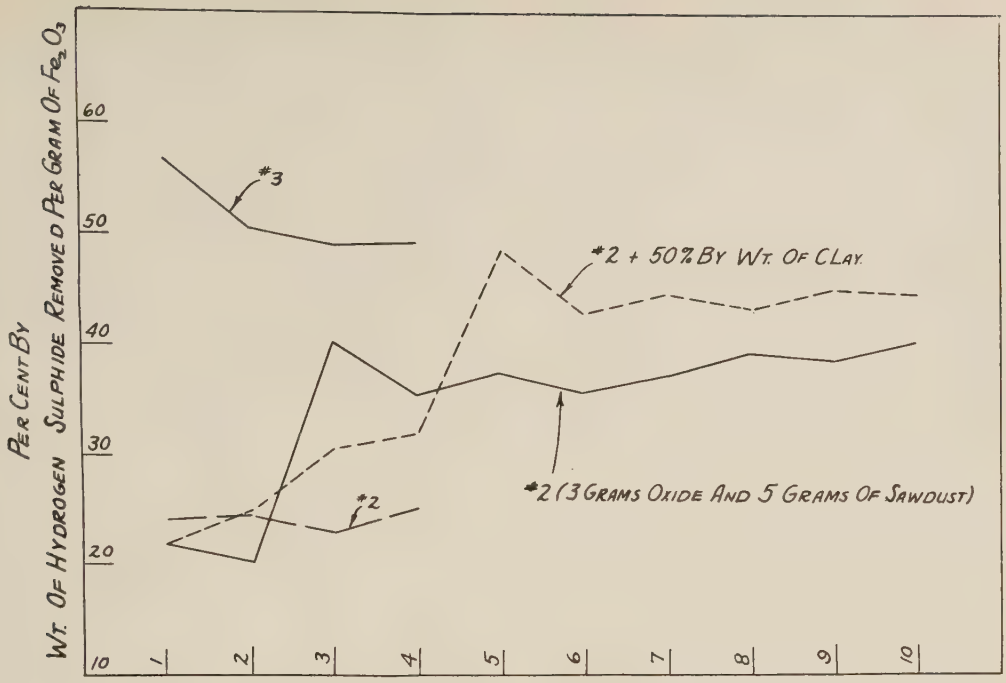

Figure 9. Consecutive daily foulings

The results of these foulings together with the foulings of oxides No. 2 alone and No. 3 alone are shown in Figure 9. It will be noted that oxide No. 2 as tested in this report had the lowest fouling. Oxide No. 2, on being mixed with greater proportions of sawdust, gave an increase in capacity and when mixed with equal proportions of Albany clay compared rather favorably with the fouling of oxide No. 3. Oxide No. 3 with increased percentage of inerts did not give an increase in capacity.

The activity of No. 2 mixed with equal proportions of clay was found to be the same as that of oxide No. 2 as received, when both were reduced to a 100 per cent ferric oxide basis.

The Rating of Purification Materials by Dye Adsorption

From the experimental facts developed in this research it appears that the ability of iron oxide purifying material to react with hydrogen sulfide and to be revivified by air, in order that this cycle be continuous, depends upon the size of the particles or the colloid content.

A method for determining this colloid content has been developed and described above. The correlation of activity and capacity with this colloid content has been indicated. From these data, a chart has been developed (Figure 10) which gives the activity, as measured in this research, from the colloid content ascertained by the method described.

Four scales for activity and one scale for dye adsorption are given. The oxides are divided into two groups. Each group is represented by two scales, one for the activity of oxides as received and the other for oxides when reduced to a 100 per cent ferric oxide basis. The use of this chart is illustrated by the key as shown, i.e., for a dye adsorption of 910 milligrams of dye the activity is about 11.5 for oxides in Group 1 on a 100 per cent ferric oxide basis. This compares favorably with samples No. 23 and No. 17 with activ

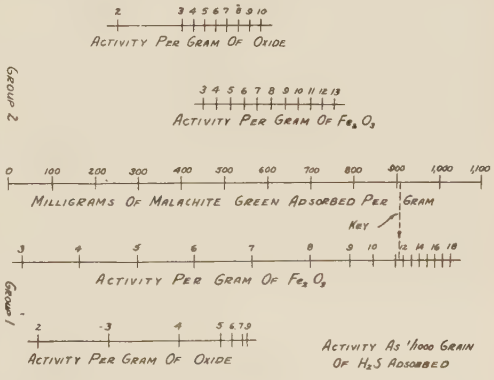
Activity Per Gram Of Oxide
Group 2
Activity Per Gram Of Fe_2O_3
Milligrams Of Malachite Green Adsorbed Per Gram
Key
Activity Per Gram Of Fe_2O_3
Group 1
Activity Per Gram Of Oxide
Activity As 1/1000 Grain Of H_2S Adsorbed

Figure 10

ties of 11.4 each and dye adsorptions of 912 milligrams and 876 milligrams, respectively. The other scales may be read in a similar manner.

It will be noted that oxides which adsorbed 251 milligrams of dye or less on an "as received" basis had low activity and inconsistent fouling and were reported by industry as indifferent. All oxides reported as favorable adsorbed more than 251 milligrams of dye and had activities in proportion to their dye adsorption. These oxides had satisfactory capacity, but this appeared to be dependent upon the size of the particle and the amount and type of inerts included in the oxide.

All oxides reported as indifferent by consumers adsorbed 307 milligrams of dye or less on a 100 per cent ferric oxide basis, while those reported as satisfactory adsorbed 421 milligrams or more.

No chart was prepared for a correlation of capacity against dye adsorption because the inclusion of various inerts (see Figure 9) caused great variation in capacity.

Discussion of Results

From the data obtained it appears that, to be satisfactory, an iron oxide purifying material must be in the colloidal form. The fine subdivision represented by colloidal particles gives the large surface necessary for satisfactory activity with hydrogen sulfide.

The oxides may be separated into two groups which show different properties for capacity and activity. These groups were designated as: Group 1—oxides containing more than 11 per cent by weight of aluminum oxide, and Group 2—oxides containing less than 11 per cent by weight of aluminum oxide.

Group 2 oxides, low in percentage of aluminum oxide, gave increasing activity with decreasing particles size; however, their activity was affected by changes in alkalinity, i.e., as the alkalinity was increased, the activity increased.

In the capacity tests as conducted herein with these oxides (Group 2), as the particle size decreased the capacity decreased. Since the reaction of iron oxide and hydrogen sulfide is exothermic, for a given amount of oxide the speed of heat liberation may be dependent upon the reaction speed or the activity; the greater the activity the higher the temperature to which the oxide will be subjected under fixed conditions. The temperature to which these amorphous particles of ferric oxide were subjected may possibly have caused these to become crystalline, as stated by Steinkopff(11).

Oxides of Group 1, containing higher percentages of aluminum oxide, also gave increasing activity with decreasing particle size. It was noted, however, that after a certain percentage of aluminum oxide was reached, reduction in alkalinity by washing did not affect the activity of these oxides. Bunte and others(12) have reported similar observations. Steinkopff(11), referring to the conversion of amorphous ferric oxide and other metallic oxides to the crystalline form by heat, does not include aluminum oxide in the group. The colloidal ferric oxide in these samples may have been prevented from changing from the amorphous to the crystalline form by the mechanical spacing of the colloidal aluminum oxide. The washing in this case might not affect the activity because the large surface offered by the ferric oxide was made possible by the insoluble aluminum oxide.

It was noted in the capacity tests that although oxides in Group 1 were subjected to approximately the same temperature as the oxides in Group 2, the capacity increased with decreasing particle size. This phenomenon may again be attributed to the mechanical spacing of the colloidal ferric oxide by colloidal aluminum oxide. Although not complete, the observations suggest that increasing percentage of colloidal aluminum oxide in colloidal ferric oxide increases the activity and capacity.

When commercially prepared oxides were heated to 550° C. for a period of one hour there was a marked change in color. This was accompanied by an increase in particle size as determined by dye adsorption and a corresponding decrease in activity and capacity. In the capacity tests with these samples it was noted that the capacity increased on successive foulings. This may possibly be explained in that the heating to 550° C. caused the particles to go from the amorphous to the crystalline state even when spaced by aluminum oxide. These crystals were apparently unstable and successive foulings may have tended to disperse these once again to the amorphous form.

When an oxide apparently formed by processes of nature was heated to 550° C. for one hour it changed color from yellow to a bright red with a corresponding increase in particle size and a decrease in activity. The capacity of this oxide was practically the same as that obtained with the sample dried at 110° C. The decrease in dye adsorption and decrease in activity indicate the formation of larger particles in the conversion of the amorphous ferric oxide to the crystalline state by heating. The high original fouling suggests that the heat of reaction caused these crystals, apparently unstable, to break down, giving a large surface resulting in the high adsorption of hydrogen sulfide. On successive foulings, with the natural oxide dried at 110° C. and 550° C., there was a great decrease in successive foulings until on the fourth fouling the capacity was but about 40 per cent of the original value. This may be explained on the assumption that the natural

oxides have the ferric oxide in such an amorphous form that on fouling this amorphous form gradually increases into the larger crystal forms of the oxide, resulting in decreased hydrogen sulfide removal. These natural oxides were all reported as indifferent in industry. The addition of sodium carbonate to these oxides, although increasing activity, did not overcome the undesirable low capacity characteristics noted with the original samples.

From these studies, it appears that oxides high in colloidal ferric oxide and low in inert content give high activity, but when fouled with gas of high hydrogen sulfide concentration, the amorphous ferric oxide tends to go to the crystalline state. Mixing this type of oxide with greater proportions of shavings, although increasing the capacity, does not completely eliminate this undesirable feature due to the impossibility of uniformily dispersing solid colloidal over non-colloidal solid substances by simple mixing. This type of oxide, when mixed with equal proportions by weight of powdered Albany clay, high in aluminum content, gave a large increase in capacity. Although the study was not conclusive, it appears that a desirable oxide may be obtained when colloidal iron oxide and aluminum oxide are in the proportions by weight of 2 to 1.

The test as developed for the determination of particle size or surface of iron oxide purifying material appears to give a satisfactory method of rating such material. It should only be used where the calcium content of the material is low. Materials with high concentrations of calcium should be washed before testing. This will tend to eliminate inconsistent dye adsorption due to the calcium.

While it is beyond the purpose of this presentation to attempt any exact economic evaluation of the test or of the explanations developed herein, it is hoped that these developments may allow industry to rate purification materials and hydrous oxides on a more consistent basis, and that the work may suggest methods which will allow purification material to be more economically used.

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BIOGRAPHY

Frank Henry Dotterweich, son of Dollie Wilson Dotterweich and the late Frank Dotterweich, was born in Baltimore, Maryland, on December 11, 1905. He attended the grade schools of Baltimore and was graduated from the Baltimore Polytechnic Institute with the A Course in June, 1923. He entered the Johns Hopkins University in September, 1925, with advanced standing, and received the degree of Bachelor of Engineering in Gas Engineering in June, 1928.

Prior to his entering the University, he was employed as an Assistant Instructor at the Baltimore Polytechnic Institute for two years. During the summer months of 1926 he was employed as a helper in the Overhead Electrical Distribution Department of the Consolidated Gas Electric Light and Power Company of Baltimore. He was engaged by the same company as an apprentice draftsman during the summer of 1927. After receiving his bachelor's degree, he was employed by the Consolidated Gas Electric Light and Power Company of Baltimore from June, 1928 to May, 1932. With this company he was employed as a Cadet Engineer, General Foreman, and Assistant to General Superintendent of Gas Operations. This work consisted in compiling data, and in calculating problems in various phases of gas operations, the major problem being an investigation of the combustion properties of gas mixtures. From June, 1932 to September, 1934 he was employed by the Playground Athletic League of Baltimore as a Leader. He has been an instructor in chemistry at the Baltimore Polytechnic Evening High School since September, 1933.

He entered the Department of Gas Engineering at the Johns Hopkins University as a graduate student in October, 1934. During his graduate work at this University he was employed as an instructor and coach in the Physical Education Department.

He is a member of the Sigma Xi.

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